

D1. Active Thermochemical Tables: Thermochemistry for the 21st Century

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Active Thermochemical Tables (ATcT) are a new paradigm of how to obtain accurate, reliable, and internally consistent thermochemistry and overcome the limitations that are deeply engrained in the traditional approach to thermochemistry. The availability of high-quality consistent thermochemical values is central to chemistry and critical in many areas, such as interpretation of kinetic measurements, development of sophisticated high-fidelity electronic structure computational treatments or development of realistic and predictive models of complex chemical environments such as combustion or the atmosphere. As opposed to the conventional sequential evolution of thermochemical values for the chemical species of interest, ATcT utilizes the Thermochemical Network (TN) approach. This approach explicitly exposes the inherent intricate interdependencies normally ignored by the conventional treatment, and allows, *inter alia*, a statistical analysis of the individual measurements that define the TN. The end result is the extraction of the best available thermochemistry, based on optimal use of all the knowledge that is available, hence making conventional tabulations of thermochemical values obsolete. Moreover, ATcT offer a number of additional features that are neither present nor possible in the traditional approach. With ATcT, new knowledge can be painlessly propagated through all affected thermochemical values. ATcT also allows hypothesis testing and evaluation, as well as discovery of weak links in the TN. The latter provides pointers to new experimental or theoretical determinations that will most efficiently improve the underlying thermochemical body of knowledge. The power of the ATcT approach is illustrated by providing significantly improved thermochemistry for several “key” thermochemical species (which are notorious for being next to impossible to improve on), together with illustration of how the ATcT paradigm impacts other recent developments in chemistry, such as experimental chemical kinetics and development of very-high-accuracy quantum-mechanical computations.

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benefited from the support and effort of the numerous past and present CMCS team members. Portions of this research are also related to the effort of a Task Group of the International Union of Pure and Applied Chemistry (2003-024-1-100), which focuses on the thermochemistry of chemical species implicated in combustion and atmospheric chemistry.

D2. On the Heats of Formation for NO, NO₂, and HO₂ and Rate Constants for OH + NO₂ → HO₂ + NO and OH + HO₂ → H₂O + O₂

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In kinetics studies by Howard on the reactions, NO + HO₂ → OH + NO₂, and its reverse, over respective temperature ranges of 232-1271 K and 452-1115 K, the heat of formation at 298 K for HO₂-radicals was determined to be 2.5 ± 0.6 kcal mole⁻¹, implying $\Delta H_{f,0K}^o = 3.2 \pm 0.6$ kcal mole⁻¹. However, the new preferred value, as obtained with the Active Thermochemical Tables approach, is $\Delta H_{f,0K}^o = 3.64 \pm 0.06$ kcal mol⁻¹. The 0.44 kcal mol⁻¹ change from the Howard value would then suggest that either the measured NO + HO₂ rate constant is low by 2 or the measured OH + NO₂ rate constant is high by 2. The NO + HO₂ reaction is of major importance in stratospheric ozone depletion, and rate constants have been measured several times and are accurately known. Hence, it is likely that the OH + NO₂ reaction is over estimated, and this supplies the motivation for the study.

The present experiments were performed with the reflected shock tube technique and OH-radical electronic absorption detection (at 308 nm) using a multi-pass optical system. The path length was 2.798 m giving high sensitivity for detection, thereby minimizing the effects of secondary reactions. Time dependent profile decays were fitted with a 23 step mechanism, but only OH + NO₂, OH + HO₂, both HO₂ and NO₂ dissociations, and the atom molecule reactions, O + NO₂ and O + C₂H₄ contributed to the decay profile. Since all of the reactions except the first two are known with good accuracy, the profiles were fitted by varying only OH + NO₂ and OH + HO₂. In all reactions, updated values for the heats of formation for NO, NO₂, HO₂, and OH from Active Thermochemical Tables have been used to evaluate equilibrium constants so that back reactions are accurately taken into account. Considering earlier work by Glaenzer and Troe (GT), the combined rate constant from the present work and GT is

$$k_{\text{OH}+\text{NO}_2} = 2.25 \times 10^{-11} \exp(-3831 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

This value is about a factor of two lower than the extrapolated direct value from Howard but agrees well with NO + HO₂ → OH + NO₂ transformed with the updated equilibrium constants. We have also re-evaluated OH + HO₂ from Troe and coworkers using updated thermodynamics and have included these data along with values derived from the present fits. We conclude that the best available experimental value for OH + HO₂ in combustion modeling applications with 1200 ≤ T ≤ 1700 K is (5 ± 3) × 10⁻¹¹ cm³ molecule⁻¹ s⁻¹.

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D3. Chemical-Kinetic Reduction In The Presence Of Diffusion

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Because much of the effort in modeling reactive flows is expended on complex chemical kinetics, it is very useful to have rational methods for the reduction of the chemical kinetics. Diffusion is an important feature of reactive flows and standard techniques for reducing chemical kinetics may break down when the time scale for diffusion competes with kinetic time scales, and new techniques have to be devised. This project is focused on understanding the way diffusion and reaction interact and to devise new reduction methods. Reduction techniques like these involve the reduction of the number of species, but a detailed understanding of the interaction of reaction and diffusion leads to other reduction methods which not only reduce the number of species, but also the spatial resolution needed in parts of the reactive flow, and these are also discussed. Both types of reduction are presented for a model of ozone combustion in the presence of diffusion.

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D4. Simulations Using Detailed Kinetics Demand Proper Resolution

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A robust method is employed to provide rational estimates of fine scale reaction zone thicknesses in one-dimensional steady gas phase detonations in mixtures of inviscid ideal reacting gases described by detailed kinetics models. Specifically, the recent results of Powers and Paolucci¹ for hydrogen-air mixtures are extended for detonations in hydrocarbon-air mixtures. Results are shown here for methane-air.

The conservation principles are cast as a set of algebraic relations giving pressure, temperature, density, and velocity as functions of species mass fractions. These are used with the kinetics equations for the evolution of N species composed of L elements to formulate the equations as a standard dynamical system of the form

$$\frac{dY_i}{dx} = f_i(Y_1, \dots, Y_{N-L}), \quad i = 1, \dots, N-L,$$

where Y_i are the species mass fractions, x is the distance coordinate, and f_i is a set of non-linear functions. These equations are integrated from a shock to an equilibrium end state. The eigenvalues of the Jacobian of f_i are calculated at every point in space, and their reciprocals give estimates of all length scales. Such a method provides a quick, rigorous, and reliable technique for estimating the necessary spatial resolution that is required in detailed computational studies of compressible reacting flows. In fact, when multidimensionality is introduced, it is likely that even finer resolution will be necessary, though the one-dimensional estimates can serve as a useful bound.

The method is illustrated using a GRI 3.0-based fifty-three species, two-hundred nineteen step model of a methane-air mixture with an initial stoichiometric distribution of $CH_4 + 2(O_2 + 3.76N_2)$ at 398 K and 1 atm. The mixture is subjected to a shock with speed 1.804×10^5 cm/s, near the CJ velocity. One can write a system of fifty-three ordinary differential equations for the evolution of the molecular species.

Figure 1 shows a plot of the evolution of the magnitudes of the resulting length scales of the system as distance varies. Many of the species formally admitted in the GRI 3.0 mechanism are near-dormant. These species induce eigenmodes with very large associated length scales; some of this behavior is visible in Figure 1, and some has been filtered. The more important finest scale is 9.2×10^{-6} cm, which occurs in the induction zone. The induction zone terminates near $x = 1.25 \times 10^0$ cm $\equiv \Delta$, the point at which the temperature gradient takes on a maximum value. At this point, vigorous chain branching and subsequent recombination commence, and the system relaxes to equilibrium soon thereafter.

The presence of fine scales alone is not a problem, but when one must simultaneously model

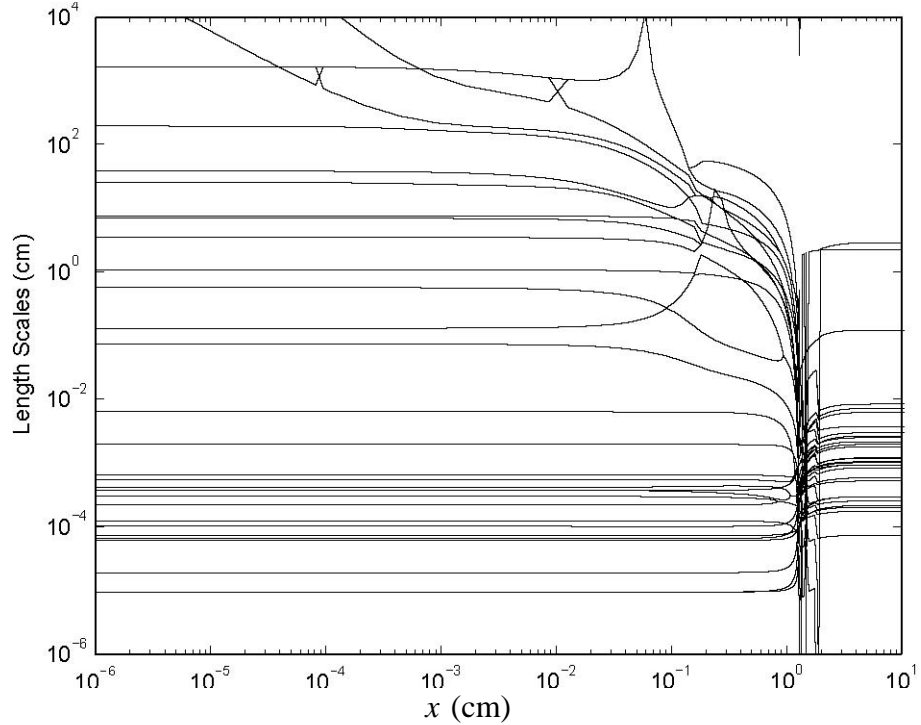


Figure 1: Reaction length scales versus distance in methane-air detonation.

much larger scales, one is faced with a truly daunting challenge. The disparity of the length scales predicted here places serious demands on existing computational methods and hardware; few calculations exist satisfying these requirements, while many employ resolutions orders of magnitude too high. However, if one wants to obtain rigorous, repeatable, grid-converged predictions from detailed models of reaction dynamics, one has no choice but to reduce the grid sizes below the scales predicted here.

Thus, our main conclusion is that most computational results available to date using detailed kinetics are not properly resolved, and subsequently, results are suspect. The finest physical length scale intrinsic to such models, $\sim 1 \times 10^{-5}$ cm, is much smaller than the discretization scale typically employed in some of the best numerical simulations, $\sim 1 \times 10^{-3}$ cm. The finest physical scale is consistent with that provided by the molecular collision theory from which the kinetics models are derived. Predictions of under-resolved numerical simulations are being artificially stabilized by numerical viscosity and do not properly capture the dynamics of the reaction zone structure. While our conclusion has been drawn in the context of a detonation problem, we speculate that similar conclusions can be drawn for a wide range of reactive flow simulations which employ detailed kinetics.

Reference

- ¹ Powers, J. M., and Paolucci, S., "Accurate Spatial Resolution Estimates for Reactive Supersonic Flow with Detailed Chemistry," *AIAA Journal*, Vol. 43, No. 5, 2005, pp. 1088-1099.

D5. *Invited:* Development Of Predictive Models For Complex Reaction Systems

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Development of predictive models for complex natural phenomena and industrial processes is at the core of scientific activity. With the present problems facing our society—threat of terrorist attacks, global warming, earthquake preparedness, safety of transport of nuclear waste, pollutant emission from automobile engines, etc.—one has to have a certain degree of confidence to rely on model predictions for political decisions, economic forecast, or design and manufacturing of automotive engines. Models of such complexity call for integration of large amounts of information, collected by numerous researchers and often from different disciplines. While collaboration among scientists is widely accepted as truism, it usually takes the form of a simple exchange of data and merging of computer codes.

The lecture will present a new approach we call *data collaboration*, which allows one to harvest substantially more of the information content of the data, incorporate experimental uncertainties into the model directly, determine realistic bounds on model predictions, rigorously assess the mutual consistency of disparate experimental observations, and discriminate among competing models. The analysis is anchored in the concept of a *dataset* that unifies all pertinent experimental data and the mechanistic knowledge for a given system, and numerical foundation based on combination of solution mapping methodology and optimization techniques advanced by robust control theory. The approach will be demonstrated using examples from combustion kinetics and biochemical reaction networks.

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Information on Data Collaboration can be found at <http://jagger.me.berkeley.edu/~pack/nsfuncertainty>.

D6. Informatics for Reaction Chemistry: The PrIMe Data Warehouse

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The PrIMe Data Warehouse is a publicly available collection of data that is currently available to the chemical community. The initial collection contains more than 100,000 records on chemical elements, bibliographies, chemical reactions and rate expressions for chemical reactions. The initial collection was formed from the NIST Chemical Kinetics Database and the GRIMech 3.0 data. All of this data is stored in a carefully designed structure. The individual data files are stored in extensible markup language (XML) format. Tools which allow searching and adding to the data warehouse are currently being developed.

In this talk, the structure of the PrIMe Data Warehouse will be explained. A brief tutorial on XML will be presented along with an introduction to the XML data formats being used in the warehouse. The importance of community participation to the PrIMe Data Warehouse will be emphasized. An overview website designed to introduce the user to the PrIMe project and allow simple views of the data warehouse will be presented.

D7. The NIST/PrIme Real Fuels Chemical Kinetic Combustion Model Database

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We report on the development status of the NIST/PrIme Real Fuels Chemical Kinetic Combustion Model Database. The goal of this Web site is to provide the combustion community with a centralized source for detailed chemical kinetic models, along with supporting data and information. We see this site as one of a set of tools under development throughout the kinetic modeling community that are directed at next generation predictive reaction modeling capabilities. The intent for this site is to be complementary to other mechanism and modeling tools under development, to facilitate collaboration among the community with regard to process modeling, and to be integrated into developing infrastructure in the chemical sciences.

The primary focus of the Web site is to provide a centralized source of information where well-documented, annotated reaction sets can be downloaded or uploaded. Particular emphasis is given towards promoting standards for nomenclature, notation, traceability, and communication in the modeling community. This includes providing systematic classification schemes for molecular species and chemical reactions. We are currently in a compilation and organization phase. Archival "flat file" listings of detailed chemical kinetic models with brief descriptions are being compiled. Input and search forms are being developed to enable users of the database to upload and download chemical kinetic models. Molecular identifiers such as CASNO's and chemical names are being compiled, along with molecular structures and other chemical information, for species of interest in combustion. A "species translator" is provided for the ad hoc, pseudo-trivial, and often cryptical symbols commonly employed to represent molecules in detailed chemical models. The lack of a commonly employed nomenclature and notation makes comparisons between different models a difficult chore at best. Tools to search, manipulate, and compare individual reactions or reactions by class for specific detailed kinetic models or among models are being developed. The bibliographic database section of the Web site is another important aspect providing supporting documentation for kinetic models, reactions, and species information.

This site is currently in its developmental stage and NIST requests comments from the community to refine and improve its content, features, and capabilities.